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3 **Revelation on the complex nature of mesoporous**
4 **hierarchical FAU-Y zeolites**
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8 Dirk Mehlhorn,¹ Jeremy Rodriguez,¹ Thomas Cacciaguerra,¹ Radu-Dorin Andrei,¹ Claudia
9 Cammarano,¹ Flavien Guenneau,² Antoine Gedeon,² Benoit Coasne,³ Matthias Thommes,⁴ Delphine
10 Minoux,⁵ Cindy Aquino,⁵ Jean-Pierre Dath,⁵ François Fajula,¹ Anne Galarneau^{1*}
11

12 ¹ICGM UMR 5253 CNRS - Univ Montpellier - ENSCM, ENSCM 240 Av Pr E. Jeanbrau, 34296
13 Montpellier cedex 5, France.
14

15 ²Sorbonne Université, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée,
16 LCMCP, F-75005 Paris, France.

17 ³Laboratoire Interdisciplinaire de Physique (LIPhy), CNRS and University Grenoble Alpes, 140 rue de
18 la Physique, Domaine Universitaire, BP 87, 38402 Saint Martin d'Herès Cedex.

19 ⁴Quantachrome Instruments, 1900 Corporate Drive, Boynton Beach, Florida 33426, United States

20 ⁵Total Research&Technology Feluy, Belgium.
21

22 *E-mail: anne.galarneau@enscm.fr
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3 **ABSTRACT:** The texture of mesoporous FAU-Y (FAUmes) prepared by surfactant-
4 templating in basic media is a subject of debate. It is proposed that mesoporous FAU-Y
5 consist of: 1- ordered mesoporous zeolite networks formed by a surfactant-assisted zeolite
6 rearrangement process involving local dissolution and reconstruction of the crystalline
7 framework, and, 2- ordered mesoporous amorphous phases as Al-MCM-41, which coexist
8 with zeolite nanodomains obtained by a dissolution-reassembly process. By the present
9 systematic study, performed with FAU-Y (Si/Al = 15) in the presence of
10 octadecyltrimethylammonium bromide and $0 < \text{NaOH/Si ratio} < 0.25$ at 115 °C for 20 h, we
11 demonstrate that mesoporous FAU zeolites consist in fact in a complex family of materials
12 with textural features strongly impacted by the experimental conditions. Two main families
13 have been disclosed: 1- for $0.0625 < \text{NaOH/Si} < 0.10$, FAUmes are ordered mesoporous
14 materials with zeolite walls, which coexist with zeolite nanodomains (100 - 200 nm) and 2-
15 for $0.125 < \text{NaOH/Si} < 0.25$, FAUmes are ordered mesoporous materials with amorphous
16 walls as Al-MCM-41, which co-exist with zeolite nanodomains (5 – 100 nm). The zeolite
17 nanodomains are decreasing in size with the increase of NaOH/Si ratio. Increasing NaOH/Si
18 ratio leads to an increase of mesopore volume, while total surface area remains constant, and
19 to a decrease of strong acidity in line with the decrease of micropore volume. The ordered
20 mesoporous materials with zeolite walls feature the highest acidity strength. The ordered
21 mesoporous materials with amorphous walls present additional large pores (50 – 200 nm),
22 which increase in size and amount with the increase of NaOH/Si ratio. This alkaline treatment
23 of FAU-Y represents a way to get ordered mesoporous materials with zeolite walls with high
24 mesopore volume for NaOH/Si = 0.10 and a new way to synthesize mesoporous Al-MCM-41
25 materials containing extra-large pores (50 – 200 nm) ideal for optimal diffusion (NaOH/Si =
26 0.25).
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30 **Keywords:** hierarchical materials, MCM-41, Faujasite, Zeolite Y, nitrogen adsorption, argon
31 adsorption, acidity, mesoporous/macroporous materials
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INTRODUCTION

Microporous materials such as zeolites have strongly impacted the refining and petrochemical industries due to their unique properties such as crystallinity, high-surface area, acidity, ion-exchange capacity, molecular sieving and shape-selectivity.¹ In catalysis however, the presence of micropores may impose internal diffusion limitations resulting in low catalyst effectiveness, pore clogging by large products or oligomers and ultimately coke formation and deactivation resulting in a decrease of productivity with time under continuous use. To increase the accessibility of the reactants to the active sites as well as the desorption of the products, creation of additional mesopores in zeolite crystals has been proposed.²⁻¹⁰ Most commonly, zeolites can be dealuminated to create large pores in the crystals, but these pores are inhomogeneous in size, often not directly connected to the exterior of the crystal and not forming a connected network inducing very low increase in diffusion, as usually assumed in the literature.¹¹ Additional techniques have been used to further increase diffusion in zeolites such as desilication in basic medium leading to mesopores connected to the exterior but inhomogeneous in size.⁸⁻¹⁰ Homogeneity of mesopore diameter has been proven to enhance mass transport in purely mesoporous materials.^{12,13} In 2005, a new procedure to synthesize mesoporous zeolites was applied by adding alkyltrimethylammonium bromide surfactants (C_nTAB, n = 10 – 22) in basic medium to create FAU-Y zeolite with homogeneous ordered mesopores like in MCM-41 materials (Hereafter FAUmes).^{14,15} It was recently suggested that, depending on the experimental conditions used, two mechanisms could operate, leading to somewhat different materials, a dissolution-reassembly process⁷ or a surfactant-assisted zeolite rearrangement process a zeolite surfactant-templating process with only local dissolution.¹⁶⁻¹⁸ In the first case, the zeolite crystal is partially dissolved and the dissolved species reassemble around surfactant micelles leading to the formation of an ordered mesoporous phase with amorphous walls as Al-MCM-41 containing additional zeolite fragments whereas in the second case the zeolite framework is mesostructured by the surfactant micelles without dissolution, leading to a zeolite with intracrystalline ordered mesoporosity free of amorphous mesoporous material. The latter can be therefore seen as a MCM-41-type architecture of mesopores built with crystalline zeolite walls of FAU-Y. In term of mesopores ordering both materials present a MCM-41-type architecture, one with amorphous walls and the other with crystalline walls. The first case has also been described as composites of (hierarchical) zeolites with ordered mesoporous materials (OMMs).^{19,20}

FAUmes feature homogeneous distributions of mesopores, due to the micelle-templated mechanism, and the interplay between the micropores and the mesopores has been proven by electron tomography²¹ and by determination of the diffusion coefficients of hexane measured by ¹H PFG NMR.²² Indeed, in mechanical mixtures of FAU-Y and MCM-41 powders (particles of ca. 10 μm each) two ¹H PFG NMR signal decays have been obtained corresponding to the diffusion in the zeolite and in the mesoporous parts. On the contrary for FAUmes only one decay was observed with a hexane diffusion coefficient intermediate between the one in pure zeolite and the one in MCM-41.²²

Different experimental conditions have been reported in the literature for the synthesis of FAUmes starting from zeolite crystals with various Si/Al ratios, using several sources of alkali (NaOH, TMAOH, NH₄OH), different temperatures (80, 115, 150 °C), different durations (12 to 24 h) and different types and amounts of alkyltrimethylammonium

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3 surfactants (CnTAX, n = 10 - 22, X = Cl, Br).^{4,14-24} In the present study, a systematic
4 investigation of the materials resulting from the transformation of FAU-Y (Si/Al = 15) into
5 FAUmes has been performed. Materials have been prepared using C18TAB as surfactant and
6 NaOH as the alkali from mixtures with molar ratios $1 \text{ SiO}_2 / n \text{ NaOH} / 0.1 \text{ C18TAB} / 50 \text{ H}_2\text{O}$
7 ($n = 0.025 - 0.25$) at 115 °C for 20 h. Our aim was to analyze precisely their structural,
8 textural and acidic properties as a function of NaOH/Si ratio. Textural and structural
9 properties of FAUmes have been analyzed by Transmission Electron Microscopy (TEM), X-
10 Ray powder diffraction (XRD), nitrogen sorption at 77 K and t-plot method,²⁵ Ar sorption at
11 77 and 87 K and by geometrical calculations using XRD and pore volumes, as previously
12 done for SBA-15 materials.^{26,27} Acidity of FAUmes materials has been measured by
13 Temperature Programmed Desorption (TPD) of ammonia.
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18 EXPERIMENTAL SECTION

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20 **Synthesis of mesoporous FAU-Y (FAUmes).** In a beaker (250 mL), x g of NaOH
21 pellets (Table 1) were added to 180 g of H₂O and the mixture was stirred with a magnet until
22 complete dissolution at 25 °C. Then 7.843 g of octadecyltrimethylammonium bromide
23 (C18TAB) were added under magnetic stirring until the complete dissolution at 25 °C. The
24 magnetic stirrer was then replaced by an endless screw stirrer, which gives a more gentle
25 stirring, necessary to keep the particle size and shape of the initial material as evidenced for
26 pseudomorphic synthesis of silica particles into MCM-41 particles.¹³ The parent zeolite (12
27 g), dealuminated H⁺-FAU-Y (Si/Al = 15) CBV720 purchased from Zeolyst was then added to
28 the preceding solution and stirred for 1-2 h at 25 °C until a homogeneous white suspension
29 was obtained. The solid recovered was then transferred into a Teflon-lined stainless autoclave
30 (250 mL) and left static for 20 hours at 115 °C. It was then filtered and washed with water
31 until neutral pH. The sample was then dried in an oven at 80 °C for 12 h and calcined at 550
32 °C for 8 h (heating rate 5 K/min). The molar ratios of the mixtures were calculated by
33 approximating FAU-Y as SiO₂: 1 SiO₂ / 0.1 C18TAB / n NaOH / 50 H₂O (Table 1).
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38 **Synthesis of mesoporous MCM-41.** Same protocole as above was used to synthesize
39 MCM-41 materials by replacing FAU-Y by fumed silica, Aerosil 200 purchased from
40 Degussa.

41 **Cationic exchange of Na⁺-FAUmes into H⁺-FAUmes for NH₃ TPD measurements.**
42 6.3 g of calcined Na⁺-FAUmes were put into 630 mL NH₄NO₃ 0.1 M in ethanol and heated
43 under reflux at 90 °C for 1 h, filtered and put again in a new solution of NH₄NO₃. This was
44 repeated 3 times. After the third cationic-exchange the material was filtered and washed 3
45 times with 200 mL of absolute ethanol. The material was dried at 80 °C overnight to obtain
46 NH₄⁺-FAUmes and calcined at 450 °C for 6 h to obtain H⁺-FAUmes.
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49 **Materials Characterization.** X-Ray Diffraction (XRD) patterns of the materials were
50 collected using a Bruker D8 Advance diffractometer with a Bragg-Brentano geometry,
51 equipped with a Bruker Lynx Eye detector and using Cu K α radiation and a Ni filter. XRD
52 patterns were recorded in the range 4 - 50° (2 θ) to identify zeolite peaks and in the range 0.04
53 - 6° to identify mesostructure organization. The angular step size was of 0.0197° and the
54 counting time of 0.2 s per step.
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3 Textural properties of the materials were determined by N₂ adsorption/desorption
4 isotherms at 77 K recorded on a Belsorb apparatus: 200-300 mg of sample were used and
5 outgassed under vacuum at 250 °C for 12 h before analysis. Broekhoff and De Boer (BdB)
6 method was applied to the N₂ desorption isotherm to calculate mesopore diameters, as
7 previously recommended for MCM-41 materials.²⁷ Micropore volumes were evaluated by
8 corrected t-plot method.²⁴ Ar adsorption/desorption isotherms were performed at 77 and 87 K
9 on an Autosorb-1C apparatus at Quantachrome: 50 mg of sample were used and outgassed
10 under vacuum at 200 °C for 20 h before analysis. Cumulative pore volume curves were drawn
11 to calculate micropore volumes using NLDFT method with a spherical model for micropores
12 and cylindrical model for mesopores.
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15 Transmission electron microscopy (TEM) images were recorded using a JEOL 1200
16 EX2 microscope operating at 100 kV at “Plateau Technique du Pole Chimie Balard
17 Montpellier”.
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19 The acidic properties of initial H⁺-FAU-Y and H⁺-FAUmes were studied by
20 Temperature-Programmed Desorption of ammonia (NH₃-TPD) using an AUTOCHEM 2910
21 apparatus from Micromeritics. The samples (40 mg) were pre-treated at 550 °C under air
22 flow (30 mL/min) for 10 min. After returning down to 100 °C the samples were saturated
23 with ammonia (45 mL/min) coming from a mixture of NH₃/He (5% NH₃) at 100 °C for 30
24 min. The weakly adsorbed NH₃ was removed by evacuation at 120 °C for 30 min in a dry
25 helium stream (25 mL/min). The ammonia desorption was carried out in helium stream (25
26 mL/min) at a heating rate of 10 °C/min up to 600 °C. The amount of desorbed ammonia was
27 monitored with a thermal conductivity detector (TCD).
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31 RESULTS AND DISCUSSION

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34 **Structural properties of FAUmes determined by XRD and TEM.** Different
35 mesoporous FAU-Y zeolites were synthesized using dealuminated H⁺-FAU-Y (Si/Al = 15) as
36 starting material. The reaction consists of a pseudomorphic transformation (meaning that the
37 particle morphology and size of the initial material is maintained during the transformation) of
38 FAU-Y into mesoporous FAU-Y (FAUmes) with MCM-41-like mesoporosity using
39 octadecyltrimethyl ammonium surfactant (C18TAB) at different molar ratios of NaOH/Si
40 (0.025 < NaOH/Si < 0.25). The resulting materials are under Na⁺ form. Each material will be
41 also referenced by its NaOH/Si ratio in the synthesis.
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44 For 0 < NaOH/Si < 0.05, XRD pattern recorded at high angles (Figure 1) show the
45 characteristic peaks of FAU-Y with a cell parameter of 2.43 - 2.44 nm. For NaOH/Si > 0.05,
46 the intensity of FAU-Y peaks decreases with the increase of the NaOH/Si ratio, meaning that
47 the amount of zeolite in the material diminishes (Figure 1).
48

49 For 0.075 < NaOH/Si < 0.125, a slight shift towards higher angle is observed for XRD
50 peaks (111), (220), (311), (331), (533), (642) (Figure 1). Such a shift would correspond to
51 unit cell parameters of 2.4085 - 2.4192 nm (Table 2), while for NaOH/Si = 0.15 no shift of
52 XRD peaks (111), (220) is observed. The shift towards higher angle can be due to a slight
53 decrease of Al content in the zeolite framework²⁸ during the transformation into FAUmes.
54 However, such values of unit cell are below the lower limit of Al amount observed for
55 dealuminated, desilicated or steamed FAU-Y, which corresponds to a₀ = 2.4265 nm. This
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3 value corresponds to the extrapolated limit value attainable for a FAU-Y zeolite free of Al in
4 its framework by using classical unit cell parameter as a function of Al atoms per unit cell
5 relationships.²⁹

6 Some other phenomena can contribute to this shift such as the decrease in size of
7 FAU-Y crystals and the formation of nanocrystals leading to a higher degree of contraction of
8 the framework.³⁰ The same effect has been observed for FAU-Y microcrystals grinded into
9 nanocrystals with a shift of the (111) and (220) XRD peaks towards higher angles for 240 and
10 120 nm nanoparticles, while for 60 nm nanoparticles no shift for (111) and (220) XRD peaks
11 was observed, but a shift towards lower angles for XRD peaks (533).³⁰ We can therefore
12 stipulate that the shift of FAU-Y XRD peaks in FAUmes is mainly due to the decrease in size
13 of the FAU-Y domains when the NaOH/Si ratio increases.

14 XRD peak intensities of FAU-Y drop to zero for $0.175 < \text{NaOH/Si} < 0.25$.

15 XRD performed at low angles (Figure 2) reveal no peak for $\text{NaOH/Si} = 0.05$
16 demonstrating that this NaOH/Si ratio is not sufficient to insure zeolite transformation into an
17 ordered mesophase.

18 For $\text{NaOH/Si} = 0.075$ and 0.10 a broad XRD peak at $2\theta = 1.7^\circ$ appears showing
19 some organization of the mesoporous network, corresponding to a hexagonal cell parameter
20 of 6.3 nm.

21 For $0.125 < \text{NaOH/Si} < 0.175$, a very well-organized hexagonal structure of
22 mesopores, as for MCM-41 materials, is observed with a first peak at $2\theta = 2.1^\circ$,
23 corresponding to a hexagonal cell parameter of 4.9 nm.

24 For higher amounts, $0.20 < \text{NaOH/Si} < 0.25$, a hexagonal mesoporous structure with a
25 cell parameter of 5.0 nm is obtained with a larger diffraction peak in comparison to $0.125 <$
26 $\text{NaOH/Si} < 0.175$, suggesting smaller domain sizes of the ordered mesophase. The XRD
27 modeling of the peak widths¹⁶ would estimate mesopore domain sizes inferior to 100 nm for
28 $\text{NaOH/Si} = 0.25$ and superior to 500 nm for $0.125 < \text{NaOH/Si} < 0.175$.

29 TEM pictures (Figure 3) show that the initial large pores (> 10 nm) with a broad pore
30 size distribution of the dealuminated zeolite FAU-Y have disappeared in FAUmes and are
31 replaced by homogeneously distributed mesopores (around 4 nm) in the whole crystal.

32 TEM pictures (Figure 3, S1) reveal also the presence of crystalline FAU-Y domains of
33 ca. 100 nm in size in FAUmes materials prepared with $0.075 < \text{NaOH/Si} < 0.125$. The size of
34 the FAU-Y nanodomains decreases with the increase of NaOH/Si ratio. These zeolite
35 nanodomains are most probably responsible for the XRD peaks of FAU-Y in FAUmes
36 (Figure 1). The size of FAU-Y nanodomains in FAUmes decreases upon increasing alkalinity,
37 from ca. 100 – 200 nm for $\text{NaOH/Si} = 0.0625 - 0.125$ to below 60 nm for higher NaOH/Si
38 ratio. The presence of FAU-Y nanodomains could be due to a heterogeneity of the aluminum
39 distribution within the crystals of the initial dealuminated FAU-Y particles composed by an
40 aggregation of crystals of different sizes and shapes. The larger crystals might be more
41 difficult to dealuminate and should be less prone to transformation in basic medium into
42 mesoporous Faujasite compared to smaller crystals.

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3 The well-organized hexagonal arrangement of mesopores revealed by XRD for $0.125 < \text{NaOH/Si} < 0.175$ is not clearly identified by TEM due probably to the large thickness of the
4 samples.
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6 By contrast, the ordered hexagonal structure is clearly observed for $0.20 < \text{NaOH/Si} <$
7 0.25 .
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9 For $0.125 < \text{NaOH/Si} < 0.25$, one can see also the formation of additional extra-large
10 pores (> 50 nm), which increase in size and amount with the increase of NaOH/Si ratio; it
11 suggests a faster dissolution rate of FAU-Y compared to the rate of formation of the MCM-
12 41-like mesostructure for high NaOH/Si ratio. The existence of these extra-large pores (50 –
13 200 nm) for $0.20 < \text{NaOH/Si} < 0.25$ explains the increase of XRD diffraction peak width by
14 the decrease of the mesopore domain size.
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17 **Textural properties of FAUmes determined from N₂ and Ar sorption isotherms.**

18 Nitrogen sorption isotherms at 77 K of FAUmes (Figure 4) show that the transformation of
19 FAU-Y into FAUmes occurs with an increase of total pore volume when NaOH/Si ratio
20 increases, while total surface area remain constant ($S_{\text{BET}} = 920 \pm 40$ m²/g) (Table 2). The
21 transformation of FAU-Y into FAUmes starts for NaOH/Si = 0.0625 evidenced by the
22 characteristic step of adsorption in the nitrogen isotherm at $p/p_0 \sim 0.42$, as expected for
23 MCM-41-like mesoporosity with similar mesopore diameters around 4 nm (Figure S2).
24 Increasing the NaOH/Si ratio leads to a shift of the adsorption step towards lower p/p_0 values,
25 meaning that mesopore diameters are decreasing. Mesopore diameters are first constant at
26 4.37 nm for $0.0625 < \text{NaOH/Si} < 0.10$ and above NaOH/Si = 0.10 mesopore diameters drop
27 continuously from 4.4 to 3.9 nm with the increase of NaOH/Si, while MCM-41 materials
28 feature a constant mesopore diameter of 3.9-4.0 nm (Tables 2, S1, Figure S3). If FAUmes is
29 considered as a MCM-41 architecture built with FAU-Y walls,¹⁶ the wall thickness e of the
30 mesostructure can be calculated from the cell parameter a of the mesostructure determined by
31 XRD and the mesopore diameter D , as for MCM-41 materials,²⁷ using the following equation:
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$$37 \quad e = a - 0.95 D \quad (1)$$

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40 FAUmes synthesized with $0.0625 < \text{NaOH/Si} < 0.10$ feature mesopore diameters of 4.37 nm
41 corresponding to wall thicknesses of 2.20 nm (Table 2) to 2.68 nm (Table S2). Such a value,
42 close to that of the unit cell of FAU, would be compatible with the existence of crystalline
43 walls of the mesophase as suggested in the case of a surfactant-assisted zeolite rearrangement
44 process. The materials consist of FAU nanodomains co-existing with an ordered mesoporous
45 zeolite.
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47 For NaOH/Si ratio above 0.10, the wall thicknesses drop abruptly to ca. 1 nm, which is too
48 thin to accommodate a FAU-Y cell and is indicative of amorphous walls. This leads to a co-
49 existence of FAU nanodomains with an ordered mesoporous phase as suggested in a
50 dissolution-reassembly process.
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52 Other features of FAUmes materials can be deduced from sorption isotherms (Figure
53 4). Large meso-/macropores (20 - 300 nm) due to the dealumination treatment of FAU-Y by
54 steaming and/or acid leaching are present in the starting FAU-Y. Some of these large
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3 inhomogeneous pores are connected to the exterior of the crystal by the micropores of the
4 zeolite, as revealed by a horizontal hysteresis between $0.43 < p/p_0 < 1$.

5 For FAUmes materials prepared with $0.025 < \text{NaOH/Si} < 0.075$, this porosity is still
6 observed. It disappears for $0.0875 < \text{NaOH/Si} < 0.125$.

7 Some new extra-large pores are formed for $0.125 < \text{NaOH/Si} < 0.25$, corresponding to
8 the large holes or white spots observed in TEM images (Figures 3, S1).

9 Some of these extra-large pores are embedded into the crystal and connected to the
10 exterior of the particles by the 4 nm mesopores, as revealed by the horizontal hysteresis
11 between $0.43 < p/p_0 < 1$ for $0.15 < \text{NaOH/Si} < 0.25$.

12 In literature^{21,31} it was shown that some of the 4 nm mesopores of FAUmes were also
13 embedded into the crystals, which are not visible by N₂ sorption at 77 K, but can be revealed
14 by Ar sorption at 77 K. These embedded mesopores have been effectively observed for
15 FAUmes materials synthesized with $0.0625 < \text{NaOH/Si} < 0.15$, as evidenced by the short
16 horizontal hysteresis starting from the desorption step of surfactant-templated mesopores,
17 corresponding to a constant volume of ca. 0.06 mL/g (Figure S4).

18 We proposed that these mesopores are embedded in between zeolite nanodomains
19 inside the crystal. For all NaOH/Si ratios, Ar adsorption isotherms at 87 K show an adsorption
20 step at low p/p_0 characteristic of FAU-Y supercages filling (Figure S4). The volume
21 associated with this step corresponds to the micropore volume, and decreases with the
22 increase of the NaOH/Si ratio. This means that crystalline domains remain intact for all
23 FAUmes materials ($0 < \text{NaOH/Si} < 0.25$), even if the XRD peaks of FAU-Y are not
24 distinguishable as for $0.175 < \text{NaOH/Si} < 0.25$ (Figure 1) due most probably to their small
25 size.

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32 The above results reveal that FAUmes materials present several features depending on
33 the NaOH/Si ratio:

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36 1- For $0.0625 < \text{NaOH/Si} < 0.25$, surfactant-templated mesopores (*ie* mesopores with uniform
37 size distributions) are formed and coexist with nanodomains of FAU-Y.
38 2- For $0 < \text{NaOH/Si} < 0.075$, presence of large pores with broad distributions of sizes due to
39 the dealumination treatment are present.
40 3- For $0.0625 < \text{NaOH/Si} < 0.15$, embedded surfactant-templated mesopores are present.
41 4- For $0.0625 < \text{NaOH/Si} < 0.10$, wall thicknesses of surfactant-templated mesopores are
42 large enough to possibly accommodate a FAU cell as suggested in the case of a surfactant-
43 assisted zeolite rearrangement process.
44 5- For $0.125 < \text{NaOH/Si} < 0.25$, wall thicknesses of surfactant-templated mesopores are too
45 thin to accommodate a FAU cell, walls are most probably amorphous. There is a change of
46 mechanism towards a dissolution-reassembly process. Extra-large pores (50-200 nm) are
47 present.
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52 Micropore and mesopore volumes (Table 3) of FAU-Y and FAUmes materials have
53 been calculated from Ar adsorption isotherms at 87 K using cumulative pore volume
54 determination (Figure S4) and by N₂ adsorption isotherms at 77 K with corrected t-plot
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method²⁴ (Figure S5). Ar and N₂ results follow the same trend with slightly larger pore volumes of 0.05 mL/g for nitrogen measurements (Table 3).

The starting FAU-Y (CBV720) used in this study is a dealuminated FAU-Y; it presents a secondary network of micro-mesopores (1.5 – 3 nm) amounting to 0.05 mL/g determined via Ar adsorption isotherm at 87 K (Figure S3). This secondary network contributes to an increase of the first slope in t-plot responsible for the slight overestimation of micropore volume (0.371 mL/g) for CBV720 calculated by t-plot with N₂ in comparison to Ar (0.300 mL/g) measurement obtained by cumulative pore volume. However if the volume of secondary network of micro-mesopores is added (0.352 mL/g) the value is close to t-plot method. Ar at 87 K and cumulative pore volume determination should be preferred to N₂ t-plot method for precise more micropore volume determination. However for comparison with literature results it is easier to use N₂ measurements.

Micropore volume of FAU-Y should not exceed 0.36 mL/g as FAU-Y present supercages volume of 0.283 mL/g and sodalite cages volume of 0.08 mL/g, the later being usually not accessible to N₂ and Ar, except when sodalite cages are opened by etching by chemical treatments as it could be probably the case for the present commercial zeolite. According to literature, the opening of sodalite cages is accompanied by the creation of 3 nm connected mesopores, as in the present case, presumably due to the merging of two supercages¹⁰ and leading to an increase of the acidity by creating accessible acid sites in opened sodalite cages.³² By treating FAU-Y with a low amount of NaOH (NaOH/Si = 0.025) these small mesopores disappear by reticulating these defects in low basic medium, resulting in an initial slight decrease of mesopore volume (Figure 5). For FAUmes synthesized with NaOH/Si > 0.05, mesopore and total volumes increase while micropore volumes decrease when the NaOH/Si ratio increases (Figure 5). The increase of the mesopore volume of FAUmes is following the same trend as the one of MCM-41 synthesized with C18TAB and different NaOH/Si ratio with a delay in NaOH/Si ratio of 0.03 (Figure S6).

Textural properties of FAUmes determined by geometrical methods. In order to gain additional insight into the complex nature of FAUmes materials, and more particularly to look into the veracity of a MCM-41 like architecture (Figure S7) with walls made of FAU-Y as proposed recently in literature,¹⁶ micropore volumes have been calculated using a geometrical calculation based on the XRD cell parameter of the mesophase and the mesopore diameter as previously done for SBA-15 materials.^{25,26} Geometrical mesopore volumes V_{mes}^g and micropore volumes V_{mic}^g (Table S3) have been determined using the mesopore diameter D_{BdB} , the cell parameter a of the mesostructure, the total pore volume V_{tot} and FAU density ρ_{FAU} (1.93 g/cm³)³³ with the following equations:

$$\varepsilon = [D_{BdB} / (1.05a)]^2 \quad (2)$$

$$V_{mes}^g = \varepsilon / [(1 - \varepsilon) \rho_{FAU}] \quad (3)$$

$$V_{mic}^g = V_{tot} - V_{mes}^g \quad (4)$$

For FAUmes synthesized with $0.075 < \text{NaOH/Si} < 0.25$, the geometrical values of mesopore volumes are extremely high, twice the volumes calculated by t-plot and Ar adsorption, leading to negative micropore volumes, which is unlikely. An explanation for this discrepancy

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3 could be a change of the density of the walls in FAUmes. However, such an assumption
4 would result in a calculated density of 4.48 g/cm^3 (calculated for FAUmes synthesized with
5 $\text{NaOH/Si} = 0.125$ for example), which is not possible as the highest possible density should
6 be 2.2 g/cm^3 as for amorphous silica or silico-aluminates.²⁷ The model of MCM-41
7 architecture with FAU-Y walls alone is therefore unlikely to describe the FAUmes materials
8 of the present study, though the existence of crystalline walls can be possible for materials
9 prepared with $0.0625 < \text{NaOH/Si} < 0.10$ (with in addition zeolitic crystalline nanodomains
10 well-dispersed in the crystal). For $\text{NaOH/Si} > 0.10$, FAUmes have to be regarded as a mosaic
11 of mesostructured amorphous domains and zeolitic crystalline nanodomains distributed over
12 the whole crystal.
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15 This assumption is fully in line with the TEM micrographs. The presence of FAU-Y
16 nanodomains in the materials explains the presence of embedded surfactant-templated
17 mesopores, which can be formed in between two FAU-Y nanodomains. The presence of these
18 FAU-Y nanodomains explains also the observation of XRD peaks of FAU-Y for FAUmes
19 synthesized with $0.125 < \text{NaOH/Si} < 0.15$, which walls cannot accommodate a FAU cell, and
20 the micropore volumes filling occurring at the same p/p_0 in Ar isotherms for all NaOH/Si
21 ratios.
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24 **Acidity of FAUmes(C18) determined by NH_3 TPD.** It is of prime importance to
25 verify if FAU-Y has kept its specific properties as its strong acidity during the transformation
26 into FAUmes. FAUmes has been synthesized in Na^+ form due to the use of NaOH as basic
27 medium. Cationic exchanges with NH_4^+ followed by calcination have been performed to
28 obtain H^+ -FAUmes. H^+ -FAU-Y has two kind of Brønsted acid sites: (1) Si-O(H)-Al groups
29 in the supercages corresponding to a FTIR band at 3630 cm^{-1} , and (2) Si-O(H)-Al groups in
30 the sodalite cages corresponding to a FTIR band at 3570 cm^{-1} . Modeling studies of the acidity
31 of FAU-Y points to a bimodal energy distribution function for both types of silanol groups,
32 where, about 64 % of the OH groups are more acidic in the supercage, while in the sodalite
33 units the figure is only about 38%.³⁴
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36 TPD of ammonia allows to readily dose the strong acidity of zeolites if a controlled
37 methodology is followed. Indeed the measure may be affected by the experimental
38 conditions,^{34,35} such as the ratio of sample weight to carrier gas flow rate, the rate of
39 temperature increase and the particles size. NH_3 desorption temperature can be governed by
40 diffusion in large particles and therefore particle sizes smaller than $160 \mu\text{m}$ are recommended.
41 In this study, all experimental conditions are the same, FAU-Y and FAUmes feature similar
42 particles size ($10 - 30 \mu\text{m}$)²² and therefore comparison of NH_3 TPD analysis can be done
43 safely. The peak of desorption at low temperature (at around 200°C) is not taken into account
44 as possible NH_3 desorption-readsorption or clustering phenomena can take place.³⁶ Only the
45 peak at high temperature ($300 - 500^\circ\text{C}$) usually associated with the strong Brønsted acidity in
46 most zeolites^{34,37} has been considered and used to characterize the strong acidity of zeolites.
47 Moreover relative amounts of strong acidity of the materials have been used and compared
48 rather than absolute values. Under appropriate conditions, good agreement between Brønsted
49 acidity determined by FTIR of adsorbed Pyridine, n-hexane cracking and the area of the high
50 temperature peak of NH_3 TPD has been observed for zeolites (BEA), with a slightly lower
51 amount of strong acidity found by NH_3 TPD.³⁸ Acidity characterization of FAUmes materials
52 using cetyltrimethylammonium as surfactant and NH_4OH as basic medium (FAUmes(C16))
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3 has been reported recently⁴ and revealed a good agreement between the relative amount of
4 strong acidity determined by NH₃ TPD (peak centered at 380-390 °C), the relative amount of
5 strong Brønsted acidity determined by CO adsorption followed by FTIR and by the area of
6 the FTIR Si-O(H)-Al supercage signal at 3630 cm⁻¹.
7

8 In the present study, NH₃ TPD profiles have been fitted with two Gaussian peaks and
9 only the peak at high temperature has been considered. The maximum of the high temperature
10 NH₃ TPD peak for initial H⁺-FAU-Y is at 380 °C and corresponds to 0.46 ± 0.03 mmol/g of
11 strong acidity (Figure S8). The intensity of the strong acidity peak decreases globally with the
12 decrease of micropore volume (Figure 6), so with the decrease of zeolite content. The
13 decrease of the number of strong acid sites on zeolites USY modified in the presence of a
14 template has also been reported by Rac et al.³⁹ The first drop of acidity between initial FAU-
15 Y and FAUmes from 0.46 ± 0.03 mmol/g to 0.30 ± 0.03 mmol/g could be ascribed to the loss
16 of accessible acid sites in initial opened sodalite cages³² by reticulation of the defects under
17 basic medium leading to only supercages acidity, which corresponds to 64% of the overall
18 strong acidity. A second drop in acidity is observed for FAUmes synthesized with NaOH/Si
19 above 0.10, when amorphous walls replace presumable crystalline walls.
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22 Interestingly, the relative amount of strong Brønsted acidity of the FAUmes(C16)
23 materials⁴ mentioned above determined by CO adsorption followed by FTIR and by the area
24 of the FTIR Si-O(H)-Al supercage bands at 3630 cm⁻¹ have been reported in Figure 6 as a
25 function of their micropore volume determined by our t-plot method. Both sets of data fit
26 perfectly a unique correlation and indicate conclusively that the origin of the strong acidity of
27 FAUmes materials is essentially (> 80%) zeolite Brønsted acidity.
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32 CONCLUSIONS

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35 Mesoporous FAU-Y materials synthesized by transformation of FAU-Y (Si/Al = 15)
36 in basic NaOH medium in the presence of octadecyltrimethylammonium surfactant at 115 °C
37 for 20 h (FAUmes) constitute a complex family of materials featuring different textural and
38 acidic properties depending on the NaOH/Si ratio used in the reacting mixture (Figure 7). The
39 transformation of FAU-Y into FAUmes with homogeneous mesopores of ca. 4 nm diameter
40 begins for NaOH/Si = 0.0625. Upon increasing the NaOH/Si ratio, the mesopore volume
41 increases and the micropore volume decreases. The transformation occurs at constant total
42 surface area. All materials contain intact FAU-Y crystalline nanodomains, which size
43 decreases by increasing NaOH/Si ratio. The strong acidity of the materials decreases with the
44 decrease of micropore volume, that is, with the decrease of the crystalline zeolite fraction.
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47 Mesoporous FAU-Y materials family feature at least 3 types of hierarchical structures:
48 FAUmes with presumably crystalline walls containing well-dispersed zeolite nanodomains
49 and an interconnected mesopore network (0.0625 < NaOH < 0.10), Al-MCM-41 like
50 materials with well-dispersed zeolite nanodomains (0.125 < NaOH < 0.175), Al-MCM-41
51 materials with an interconnected macroporous network. Two materials would be very
52 promising for applications needing high diffusivity: FAUmes prepared with NaOH/Si = 0.10
53 featuring large mesopore volume and high acidity, and Al-MCM-41 prepared with NaOH/Si
54 = 0.25 featuring large macropore volume and mild acidity.
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6 isotherms data for the t-plot calculations of FAUmes(C16).
7

8 **Supporting Information:** Additional TEM of FAUmes, N₂ sorption isotherms of MCM-41
9 materials and characterization, Ar isotherms of FAUmes at 87 and 77 K, t-plot corrections
10 formula, NH₃ TPD spectra.
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Table 1. Amount of NaOH used in the synthesis of FAUmes.

n NaOH (mol)	x NaOH (g)
0.025	0.199
0.05	0.399
0.075	0.599
0.1	0.799
0.125	0.999
0.15	1.198
0.175	1.398
0.20	1.598
0.25	1.998

Table 2. XRD and N₂ sorption isotherms results of FAUmes as a function of NaOH/Si ratio used in the synthesis: a_0 cell parameter of FAU-Y-like microporosity, a cell parameter of the MCM-41-like mesoporosity, D_{BdB} mesopore diameter, e wall thickness, specific surface area S_{BET} , total pore volume V_{tot} .

NaOH/Si	a_0 (nm)	a (nm)	D_{BdB} (nm)	e (nm)	S_{BET} (m ² /g)	V_{tot} (mL/g)
0	2.428	none	-	-	937	0.431
0.025	2.434	none	-	-	868	0.478
0.05	2.437	none	4.30	-	861	0.437
0.075	2.408	6.35	4.37	2.20	894	0.534
0.10	2.416	6.35	4.37	2.20	926	0.634
0.125	2.419	4.94	4.34	0.82	957	0.714
0.15	2.434	4.94	4.24	0.91	949	0.766
0.175	none	4.70	4.14	0.77	960	0.782
0.25	none	5.09	3.91	1.38	954	0.811

$$a = (2/(3))^{1/2}d_{100}, e = a - 0.95 D_{\text{BdB}}$$

Table 3. Micropore and mesopore volumes of FAUmes synthesized with different NaOH/Si ratio obtained by nitrogen adsorption isotherms at 77 K and Ar adsorption isotherms at 87 K.

NaOH/Si	V _{tot} (Ar) mL/g	V _{mic} (Ar) mL/g	V _{mes} (Ar) mL/g	V _{tot-tpt} (N ₂) mL/g	V _{mic-tpt} (N ₂) mL/g	V _{mic-cor} (N ₂) mL/g	V _{mes-cor} (N ₂) mL/g
0	0.378	0.300	0.078	0.431	0.265	0.371	0.060
0.025				0.383	0.258	0.361	0.022
0.05				0.437	0.233	0.326	0.111
0.0625				0.479	0.222	0.311	0.168
0.075	0.497	0.249	0.248	0.534	0.209	0.280	0.254
0.0875				0.592	0.190	0.242	0.350
0.10	0.581	0.208	0.373	0.634	0.180	0.222	0.411
0.125	0.657	0.170	0.487	0.714	0.149	0.170	0.544
0.15	0.718	0.130	0.588	0.766	0.116	0.122	0.644
0.175				0.782	0.102	0.103	0.678
0.20				0.790	0.085	0.085	0.705
0.25	0.748	0.055	0.693	0.811	0.057	0.057	0.754

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3 **Figure captions**
4

5 **Figure 1.** XRD pattern (high angles) of FAUmes prepared with different NaOH/Si ratio.
6 Inset. Magnification of (220) XRD peak of FAU-Y.
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8
9 **Figure 2.** XRD pattern (low angles) of FAUmes prepared with different NaOH/Si ratio.
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11 **Figure 3.** TEM of FAUmes prepared with different NaOH/Si ratio. Rectangle evidences
12 FAU-Y nanodomains.
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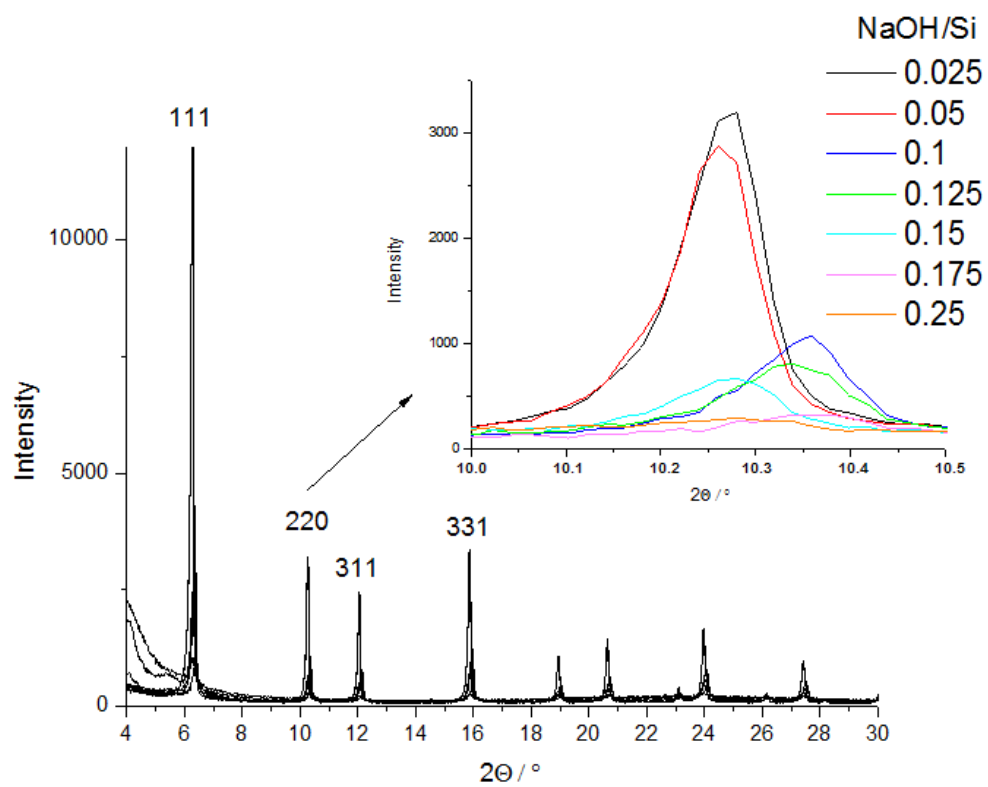
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15 **Figure 4.** Nitrogen sorption isotherms at 77 K of FAUmes prepared with different NaOH/Si
16 ratio.
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19 **Figure 5.** Total pore volumes, mesopore volumes and micropore volumes of FAUmes
20 prepared with different NaOH/Si ratio determined by N₂ adsorption at 77 K with corrected t-
21 plot method.
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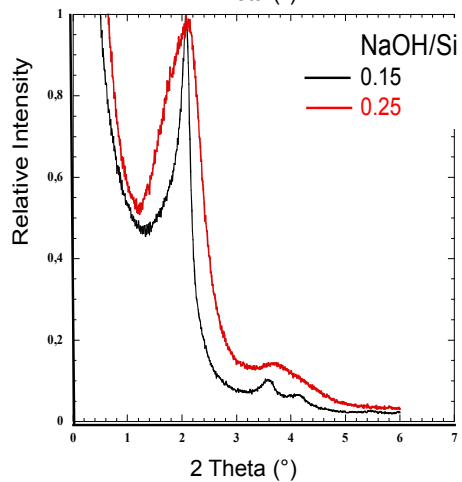
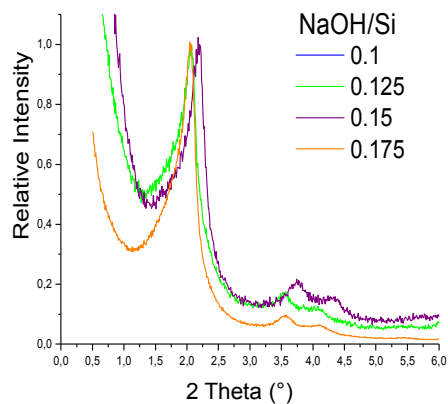
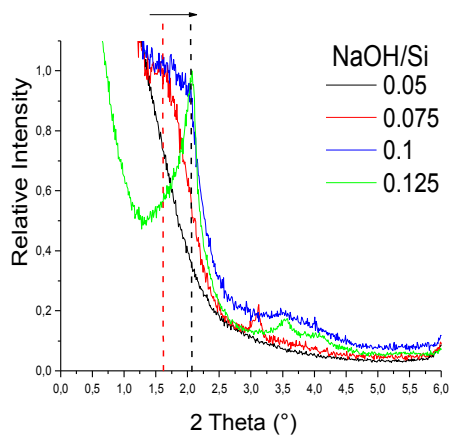
23
24 **Figure 6.** Relative amount of strong acidity determined by NH₃ TPD (circle) as a function of
25 micropore volume and comparison with literature⁴ results (square): relative strong Brønsted
26 acidity of FAUmes determined by CO-FTIR (red) and by FTIR band intensity of SiO(H)Al in
27 supercages (blue). Initial strong acidity of FAU-Y CBV720: 0.46 mmol/g.
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30 **Figure 7.** Schematic representation of FAUmes materials as a function of NaOH/Si ratio used
31 in the synthesis.
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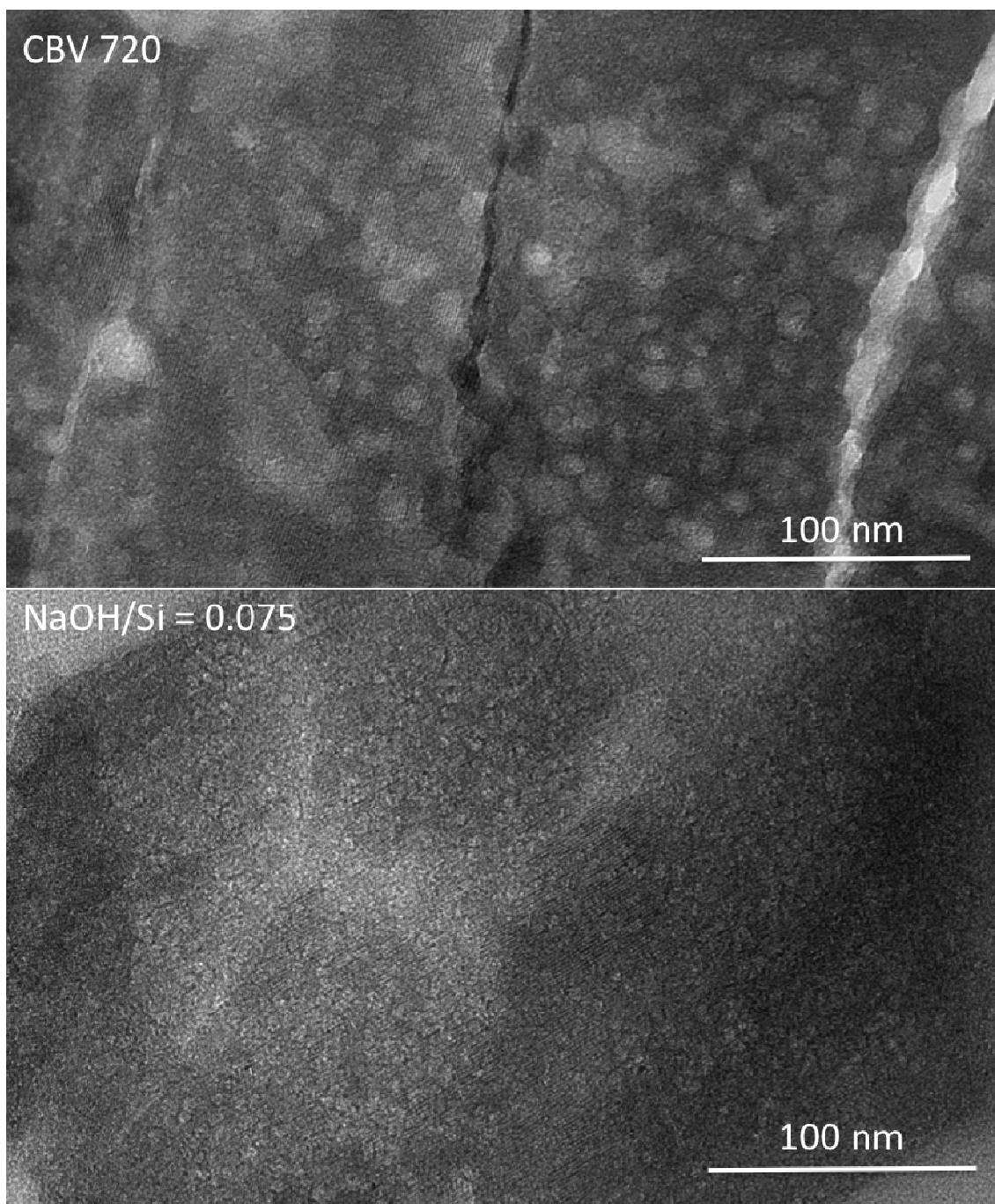
Figure 1



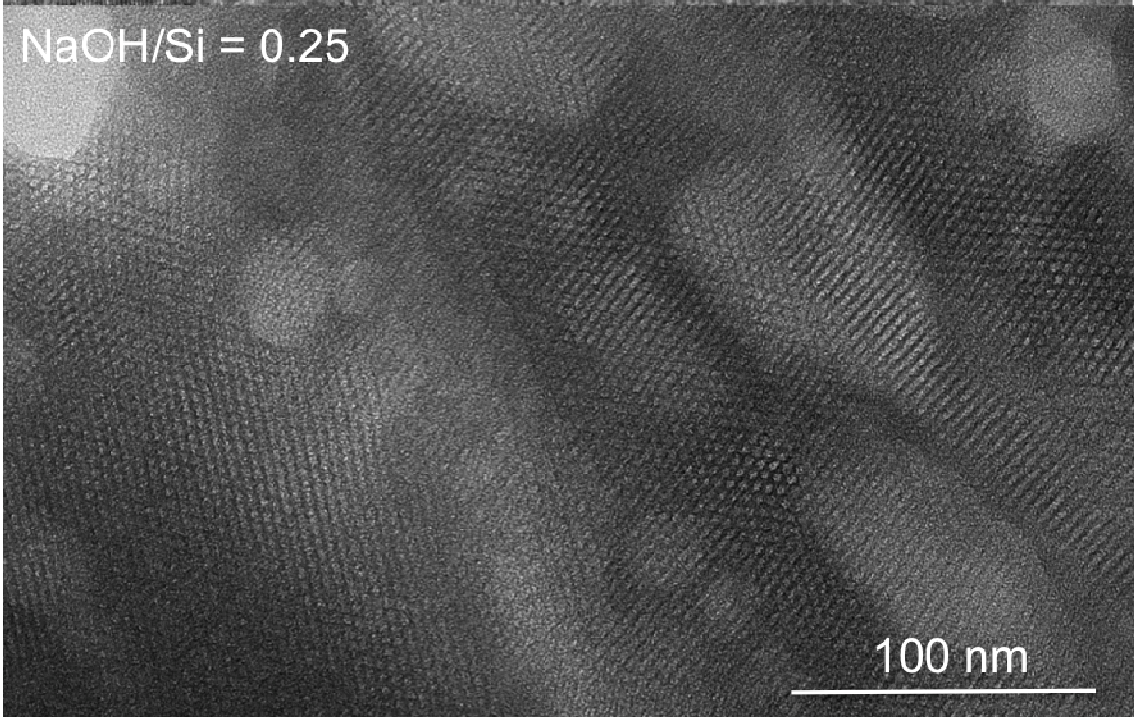
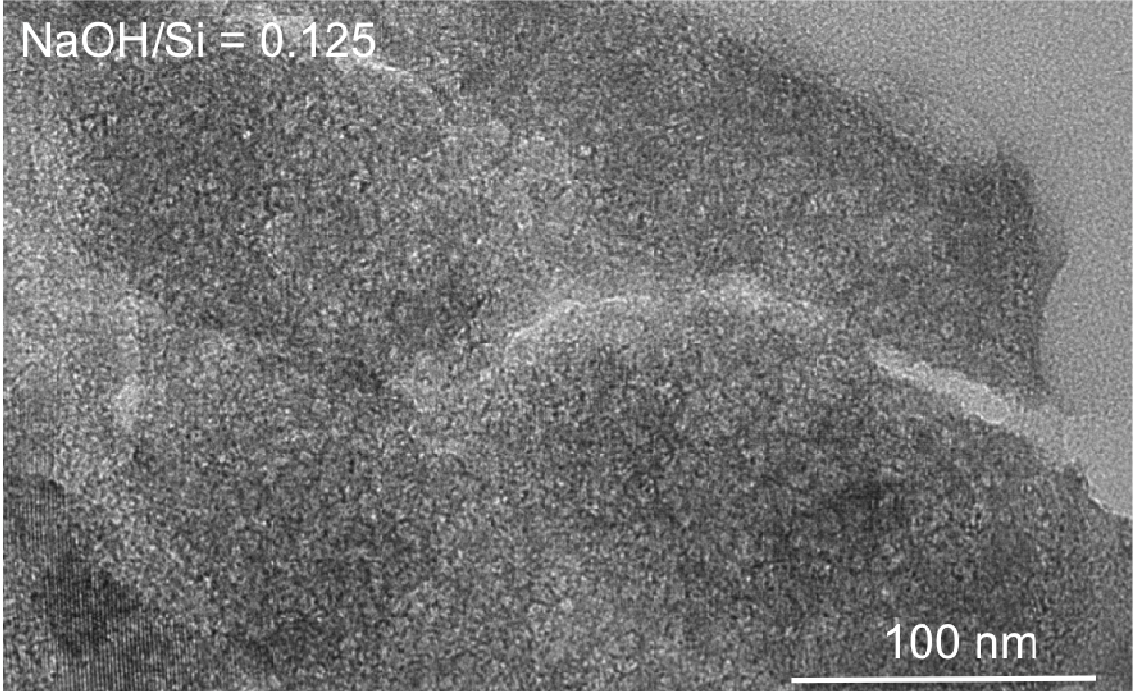
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4 **Figure 2**
5 **Required parameters are missing or incorrect.**
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5 **Figure 3**
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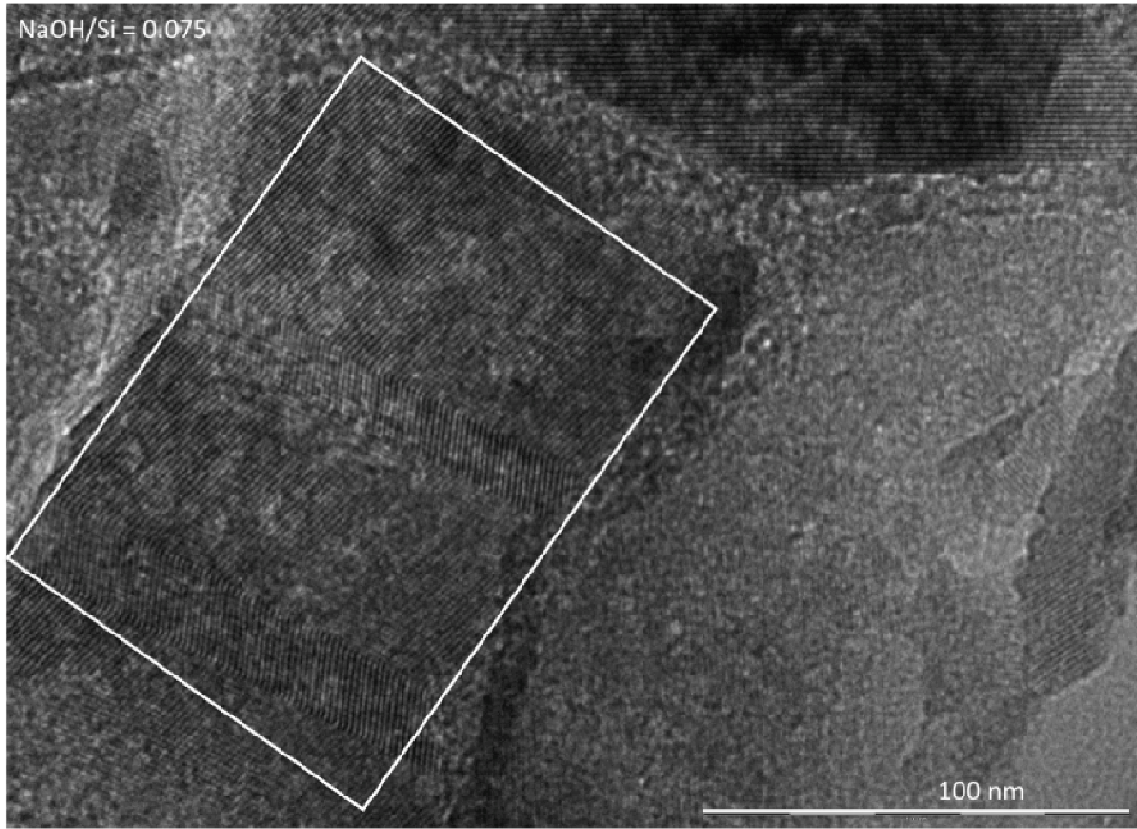


Figure 5

Required parameters are missing or incorrect.

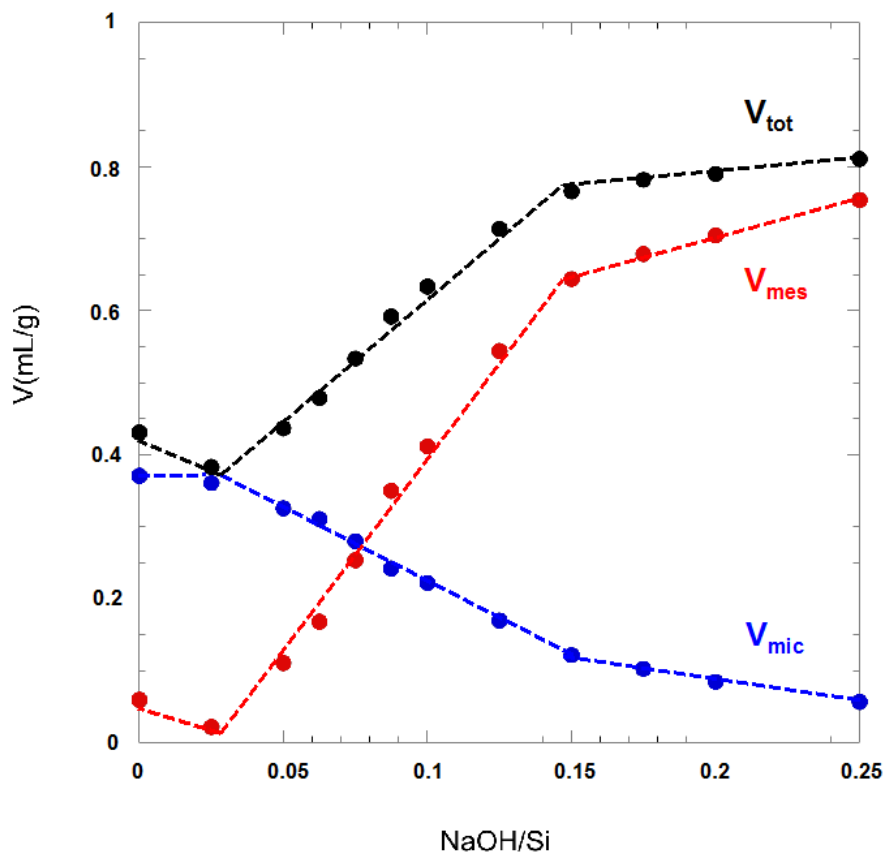


Figure 6

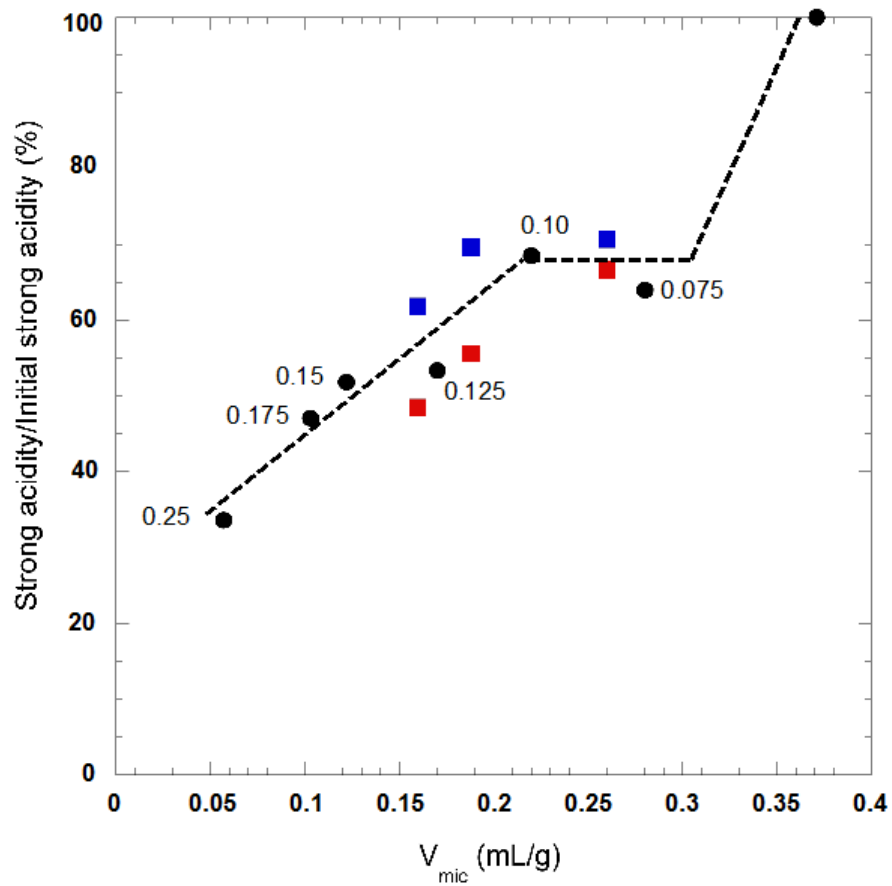
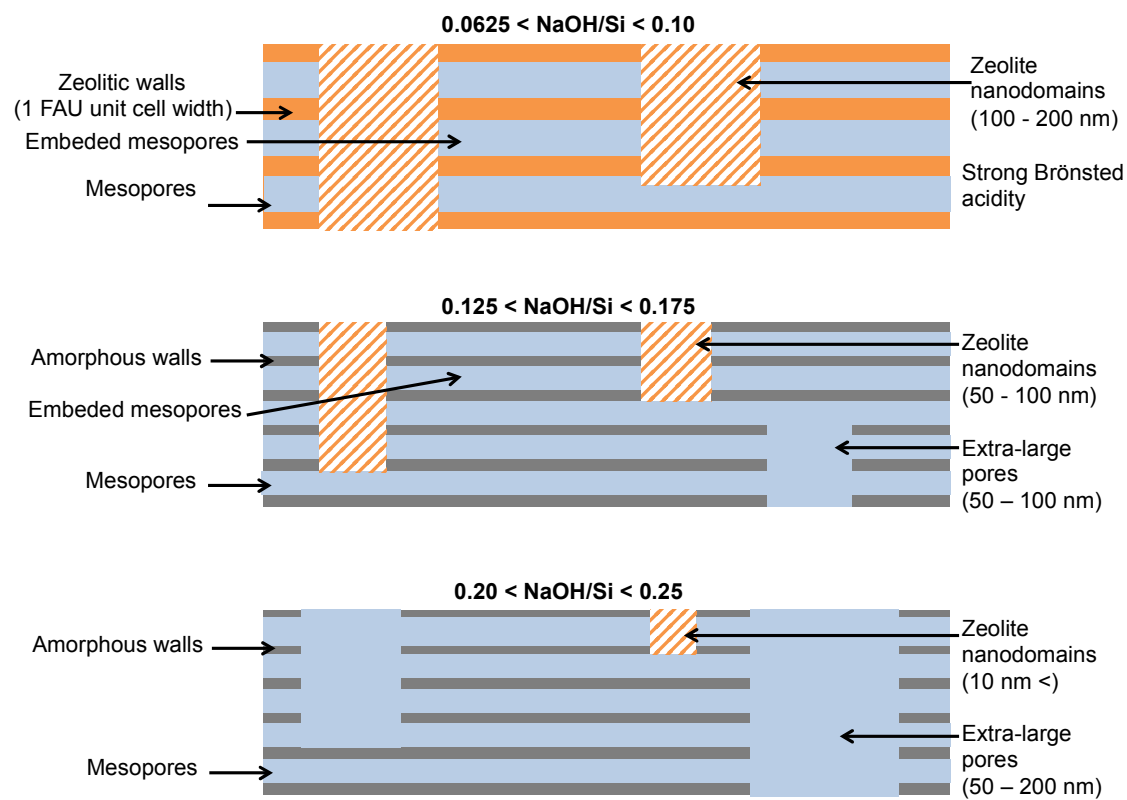


Figure 7



Graphical Abstract

